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THE DETERMINATION OF THE POTENTIAL CONSTANTS OF SO_2 FROM CENTRIFUGAL DISTORTION EFFECTS*

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Abstract

The microwave spectrum of SO_2 was reanalyzed with particular emphasis upon the effect of centrifugal distortion. It was possible to fit the rotational spectrum to within a mean deviation of ± 0.23 Mc using the energy expression given by Kivelson and Wilson.[7] The rotational constants so determined are a = 60778.79 Mc, b = 10318.10 Mc and c = 8799.96 Mc. The four distortion constants could not be uniquely determined directly from the rotational spectrum.

The sets of potential constants determined by Wilson and Polo[12] were used to calculate distortion constants and these in turn used to calculate frequency shifts due to centrifugal distortion. These shifts are critically dependent upon the set of potential constants used. By choosing a set of potential constants that yields distortion frequencies in accord with those obtained from a direct analysis of the rotational spectrum, a very sensitive determination of the potential constants may be made. The resulting distortion constants are: $\tau_{aaaa} = -9.8098$ Mc; $\tau_{bbbb} = -0.039697$ Mc; $\tau_{aabb} = +0.41170$ Mc; $\tau_{abab} = -0.053204$ Mc.

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INTRODUCTION

The microwave spectrum of SO_2 has been studied previously by several investigators.[1,2,3] Crable and Smith[2] studied the low J transitions and determined structural parameters on the basis of a rigid rotor model. Sirvetz considered high J transitions using a semi-rigid model with constants of centrifugal distortion calculated from infrared vibrational data. The present investigation treats the SO_2 spectrum in a third way; it also employs a semi-rigid rotor model, but the constants of centrifugal distortion are determined directly from the rotational spectrum and used to obtain estimates of the vibrational frequencies. Finally, the information obtained from the pure rotational spectrum is combined with results derived from the vibrational spectrum to give precise information about the quadratic force field.

The Hamiltonian in the symmetric rotor representation for a semi-rigid rotor of orthorhombic symmetry is a complicated matrix[4] with $(K|K)$, $(K|K \pm 2)$ and $(K|K \pm 4)$ elements where K is the quantum number corresponding to the component of angular momentum along the z-axis. Sirvetz used the Mathieu function method proposed by Golden[5] to evaluate the contribution of the $(K|K \pm 4)$ elements and the continued fraction method discussed by King, Hainer

[1] Dailey, Golden, and Wilson, Phys. Rev. 72, 871 (1947).

[2] G. Crable and W. Smith, J. Chem. Phys. 19, 502 (1951).

[3] M. Sirvetz, J. Chem. Phys. 19, 938 (1951).

[4] E. B. Wilson, Jr., J. Chem. Phys. 5, 617 (1937).

[5] S. Golden, J. Chem. Phys. 16, 250 (1948); and erratum, ibid. 17, 586 (1949).

and Cross[6] to evaluate the contribution arising from the rest of the energy matrix. Since the constants of centrifugal distortion appear both on and off the diagonal in the Hamiltonian matrix used above, it would be an almost impossible task to determine these constants empirically from the rotational spectrum without making some approximations.

[6] King, Hainer and Cross, J. Chem. Phys. 11, 27 (1943).

Recently an approximate form of the Hamiltonian for the semi-rigid rotor has been proposed.[7] In this form the effect of centrifugal distortion on the energy levels may be treated as an additive perturbation in which the distortion constants (τ's) enter linearly. This form permits the determination of the τ's from rotational data.

[7] D. Kivelson and E. B. Wilson, Jr., J. Chem. Phys. 20, 1575 (1952). Hereafter referred to as I.

THEORY

The energy of a semi-rigid rotor is given by Eq. (I-17). Rewriting this equation in a more convenient form one has:

$$\begin{aligned} W = W_o &- [D_J + 2R_6]\, J^2(J+1)^2 - [D_{JK} - 4R_6]\, J(J+1)\langle P_z^2\rangle \\ &- [D_K + 2R_6]\langle P_z^4\rangle + 2\sigma\delta_J\, J(J+1)\,(p_z^2 - \eta) \\ &+ 4R_5\sigma(-p_z^4 + K^2\eta + K^2 p_z^2 + p_z^2\eta) \\ &+ 4R_6\sigma^2\,(p_z^4 - 2K^2 p_z^2 + \eta^2 - 2p_z^2\eta) \end{aligned} \tag{1}$$

where

$$p_z^2 = \langle P_z^2\rangle - K^2 \tag{2}$$

$$p_z^4 = \langle P_z^4 \rangle - K^4 \tag{3}$$

$$\eta = \frac{2\lambda}{3 - \varkappa} - K^2 \tag{4}$$

$\varkappa$ is the asymmetry parameter and λ the reduced energy defined by King, Hainer and Cross,[6] K is the limiting symmetric rotor quantum number and the remaining quantities in Eq. (1) are defined in I.

The distortion constants appearing in Eq. (1) are linear combinations of the distortion constants $\tau_{\alpha\beta\gamma\delta}$ introduced by Wilson and Howard.[8] Explicit formulas for the evaluation of these τ's in terms of the four independent force constants of SO_2 have been given in a previous paper.[9] Since there are only four force constants, the seven τ's that enter into Eq. (1) are connected, the relations being as follows:

[8] E. B. Wilson, Jr. and J. B. Howard, J. Chem. Phys. 4, 260 (1936).

[9] D. Kivelson and E. B. Wilson, Jr., J. Chem. Phys. 21, 1229 (1953).

$$\tau_{yyyy} = \tau_{xxxx}\frac{c^4}{b^4} + \tau_{zzzz}\frac{c^4}{a^4} + 2\tau_{xxzz}\frac{c^4}{a^2b^2} \tag{5}$$

$$\tau_{yyxx} = \tau_{xxxx}\frac{c^2}{b^2} + \tau_{xxzz}\frac{c^2}{a^2} \tag{6}$$

$$\tau_{yyzz} = \tau_{zzzz}\frac{c^2}{a^2} + \tau_{xxzz}\frac{c^2}{b^2} \tag{7}$$

where a, b, c are the usual reciprocal principal moments of inertia, $a \geq b \geq c$ and the I^r representation of King, Hainer, and Cross has been used.

Combining Eqs. (5) - (7) with Eq. (1) one finds that the energy of the system is equal to the rigid rotor energy (W_o) plus terms linear in the four distortion constants τ_{xxxx}, τ_{zzzz}, τ_{xxzz}, τ_{xzxz}. The coefficients of

these constants can be readily calculated since J and K are the rotational quantum numbers, λ is the rigid rotor reduced energy and can be calculated from previously determined approximate rigid rotor parameters, and $\langle P_z^2 \rangle$ and $\langle P_z^4 \rangle$ can be calculated from the rigid rotor parameters by means of Eq. (I-23).

ITERATION PROCEDURE

The rigid rotor parameters determined by Crable and Smith from the three lowest J transitions which are only slightly affected by centrifugal distortion, were used as zeroth-order rotational constants. The four highest J transitions were then calculated on this basis and the discrepancy between calculated and observed frequencies ($\delta\nu$) was attributed to centrifugal distortion. $\langle P_z^2 \rangle$ and $\langle P_z^4 \rangle$ were calculated using these parameters and Eq. (1) was used to solve for the four independent τ's. The distortion of the three lowest J transitions was then computed and new rigid rotor parameters determined. The procedure was then repeated with these parameters. The initial coefficients of the τ's were used throughout since the change in rigid rotor parameters did not affect these quantities appreciably. The cycle was repeated three times. The mean deviation between the observed frequencies and those calculated by this method is 1.25 megacycles for all these lines.

A least squares calculation on seven of the levels with the four τ's as parameters did not reduce the mean deviation. Since the reported mean experimental[2] error on the three lowest J lines is .12 Mc. and the mean discrepancy between the present calculation and observed values for these lines is .15 Mc it was not thought profitable to continue the iteration procedure.

The rotational parameters determined in this manner are

$$a = 60778.79 \text{ Mc.}$$

$$b = 10318.03 \text{ Mc.}$$

$$c = 8799.74 \text{ Mc.}$$

which are respectively 2 2, 0.4, and 0.3 megacycles larger than those reported by Crable and Smith.

LEAST SQUARES PROCEDURE

In order to get a more reliable set of constants a more extended least squares calculation was carried through with seven variables, the four distortion constants and three functions of the rotational constants. The rigid rotor energy was differentiated with respect to the rotational parameters and only linear variations of the energy with respect to these parameters were considered.[10] It is convenient to take (a-c), (b+c) and the asymmetry parameter κ as the rigid rotor variables. The least squares calculations were performed on a system of eleven lines, that is all but the $4_{04} \rightarrow 4_{13}$ and the $9_{19} \rightarrow 8_{26}$ lines in Table I. The resulting rigid rotor parameters are:

$$a = 60778.79 \text{ Mc.}$$

$$b = 10318.10 \text{ Mc.}$$

$$c = 8799.96 \text{ Mc.}$$

[10] The rigid rotor energy W_o is given by the relation

$$W_o = (1/2)\,(b+c)\,J(J+1) + (1/2)\,(a-c)\,\lambda(\kappa)$$

where $\lambda(\kappa)$ is the reduced energy. With the use of $\partial W_o/\partial a = \langle P_z^2 \rangle$ it can be shown that

$$d\lambda/d\kappa = (\lambda - 2\langle P_z^2 \rangle)/(1+\kappa)$$

$\langle P_z^2 \rangle$ can be evaluated by Eq. I-23.

and the distortion constants are given in Table II. The transition frequencies calculated on the basis of these parameters are given in Table I along with the observed frequencies. These agree much better with the observed frequencies than do the preceding set. The mean deviation from the experimental frequencies is 0.23 Mc., which is just above the range of experimental accuracy.

RESULTS

Table II gives the values of the τ's determined by the procedures outlined above. It is found that the relations between the τ's and the frequencies are not sufficiently independent to permit the determination of a unique set of τ's, although one may obtain τ's that yield frequencies in good agreement with the observed microwave frequencies. Since the τ's can be explicitly related to the force constants that enter into a general quadratic potential field,[9] (cf. Appendix) the force constants corresponding to the various sets of τ's have been evaluated and are given in Table II.[11] The interatomic parameters used were derived from

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[11] In making these and subsequent calculations the following constants were used: $c = 2.997902 \times 10^{10}$ cm./sec.; $N = 6.02544 \pm .00011 \times 10^{23}$ gm. mole^{-1}; $m_o = 16$ AMU; $m_s = 31.9823$ AMU; $h = 6.62377 \pm .00018 \times 10^{27}$ erg. sec.

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the "effective"inverse moments of inertia a and b. They turn out to be $d_{s-o} = 1.4321$ Å and $\measuredangle$O-S-O=119.536°.The force constants have been used to calculate the vibrational frequencies of SO_2. These results are given in Table II.

The predicted vibrational frequencies are the right order of magnitude but differ appreciably from the observed values. This is understandable since the various sets of τ's calculated from the rotational spectrum yield quite different vibrational frequencies. Thus very great accuracy could not be expected since a unique set of τ's cannot be determined from the rotational spectrum and

since centrifugal distortion only adds a small correction term to the rotational energy. Even for diatomic molecules the agreement is not better than twelve percent.[12]

[12] G. Herzberg, "Rotation and Vibration of Diatomic Molecules," D. Van Nostrand Co., Inc. (1950). p. 105.

The effect of centrifugal distortion on the rotational frequencies of SO_2 is small even for high J values. Thus a small error in the microwave frequency introduces a large error in the τ's and hence in the vibrational frequencies. It should be noted that although the frequency shift of the lines arising from distortion is small, the corresponding shift in the energy levels is large, e.g., about 7000 Mc. for $35_{6,30}$. The τ's have been reported to many places in spite of the fact that even the second place is in doubt because the distortion frequencies depend on rather small differences of large numbers.

COMBINED INFRARED-MICROWAVE RESULTS

Microwave data together with infrared measurements can be combined to yield more information concerning the force field than can be obtained from either approach individually. In the preceding paper Polo and Wilson[13] have analyzed

[13] S. Polo and M. K. Wilson; see preceding paper.

the infrared spectra of O^{16}-S-O^{16} and of O^{16}-S-O^{18} and have obtained potential constants describing a general quadratic force field. However, the infrared data allow the determination of the potential constants only within a range of values corresponding to $F_{11} = (10.0 \pm 0.2) \times 10^5$ dynes cm.$^{-1}$

These potential constants have been used to compute the four independent τ's entering into the expression for the frequency shift due to centrifugal distortion. This is the reverse of the process described in the previous sections of this paper. The τ's were computed for each of three sets of potential constants obtained by Polo and Wilson, for the set corresponding to $F_{11} = 9.8 \times 10^5$, 10.0×10^5, 10.2×10^5 dyne cm.$^{-1}$ The frequency shift due to distortion was then calculated for each set of distortion constants. In Table III it is readily seen that the distortion frequencies depend critically upon the particular set of constants used. It is difficult to decide exactly what the distortion frequency should be but also included in Table III are the distortion frequencies calculated from the two sets of τ's derived directly from the rotational spectrum. (See Table II). This should give an estimate of the uncertainty in the frequency shift due to centrifugal distortion. Even without too much precision in estimating the "true" distortion frequencies, it can be seen that the correct set of potential constants can be obtained with great accuracy by interpolation. Thus the best value of F_{11} can be set at $10.030 \pm .005$/ x 10^5 dyne cm.$^{-1}$ Using this value of the potential constant, the other potential constants were obtained from the infrared data, the τ's rederived and the distortion frequencies recalculated. The force constant[14] turn out to be

[14] See definition given in reference 12.

$$f_d = 10.006 \pm .0025 \times 10^5 \text{ dyne cm.}^{-1}$$

$$f_{\alpha/d_b^2} = 0.7933 \pm .00015 \times 10^5 \text{ dyne cm.}^{-1}$$

$$f_{dd} = 0.0236 \pm .0025 \times 10^5 \text{ dyne cm.}^{-1}$$

$$f_{dx/d_b} = 0.189 \pm .005 \times 10^5 \text{ dyne cm.}^{-1}$$

while the distortion constants are

$$\tau_{aaaa} = -9.8098 \text{ Mc.}$$
$$\tau_{bbbb} = -0.039696 \text{ Mc.}$$
$$\tau_{aabb} = +0.41170 \text{ Mc.}$$
$$\tau_{abab} = -0.053203 \text{ Mc.}$$

Table III gives the distortion frequencies calculated with these constants. The mean deviation between the observed frequencies and the frequencies calculated with these constants is 1.32 Mc. for all the transitions considered.

DISCUSSION

It has been seen that Eq. (1) can be used to yield calculated frequencies in very good agreement with the observed microwave frequencies of SO_2. However, no unique set of τ's can be obtained in this way, and the derived vibrational frequencies differ considerably from the observed infrared frequencies. At the same time it is seen that if the τ's are to be calculated from force constants derived from the vibrational frequencies, the force constants must be known with great accuracy for the resulting distortion frequencies depend critically on the values of force constants used. This accounts for the difficulty Sirvetz[3] had in fitting the rotational spectrum of SO_2.

The infrared data[13] were used to yield interrelations between the potential constants. In this way the problem was reduced to a one parameter one which could be determined accurately by the analysis of the effect of centrifugal distortion in the rotational spectrum. In this way accurate values of the potential constants could be obtained. The accuracy reported is somewhat deceptive since it assumes that the theory is exact when in fact such factors as the

anharmonicity of the potential function has been totally omitted. The use of a, b, and c in Eqs. (5)-(7) rather than the equilibrium values of the moments of inertia and the use of non-equilibrium interatomic parameters also affects the results. Furthermore, the accuracy of the interrelations of the force constants determined from the infrared results are limiting factors on the final precision.

The methods used in this analysis are quite general and should be applicable to other molecules although the calculations become quite formidable for more complicated molecules.

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APPENDIX

The distortion constants are related to the potential constants as follows:[9]

$$-R\tau_{aaaa}\, a^{-2} = 2F_{11}^{-1} + \tan^2\theta\, F_{22}^{-1} - 2\sqrt{2}\, \tan\theta\, F_{12}^{-1}$$

$$-R\tau_{bbbb}\, b^{-2} = 2F_{11}^{-1} + \operatorname{ctn}^2\theta\, F_{22}^{-1} + 2\sqrt{2}\, \operatorname{ctn}\theta\, F_{12}^{-1}$$

$$-R\tau_{zzbb}\, a^{-1} b^{-1} = 2F_{11}^{-1} - F_{22}^{-1} + \sqrt{2}\, (\operatorname{ctn}\theta - \tan\theta)\, F_{12}^{-1}$$

$$-R\tau_{abab}\, a^{-1} b^{-1} = 2Mm_s^{-1} (1 + 2m_o m_s^{-1} \sin^2\theta)^{-2} F_{33}^{-1}$$

where

$$R = \tfrac{1}{2}\, d^2 h^{-1} 10^{-22}$$

θ is one-half the O-S-O angle and d is the S-O distance expressed in Angstrom units and $M = 2m_o + m_s$. $\underline{F}^{-1}$ is the inverse of the potential constant matrix $\underline{F}$ given by Polo and Wilson.[13]

TABLE 1

SO_2 ROTATIONAL TRANSITIONS

Transition	Computed Frequency "Least Squares Method" (Mc.)	Observed Frequency (Mc.)
$0_{0,0} \rightarrow 1_{1,1}$	69576.01	69576.06[a]
$2_{0,2} \rightarrow 2_{1,1}$	53529.00	53529.16[a]
$3_{1,3} \rightarrow 4_{0,4}$	29321.44	29321 22[a]
$4_{0,4} \rightarrow 4_{1,3}$	59224.96	59225.00[a]
$6_{1,5} \rightarrow 5_{2,4}$	23414.08	23414.30[b]
$7_{2,6} \rightarrow 8_{1,7}$	25393.22	25392.80[b]
$9_{1,9} \rightarrow 8_{2,6}$	24083.65	24083.39[b]
$13_{2,19} \rightarrow 12_{3,9}$	20335.07	20335.47[b]
$16_{3,13} \rightarrow 17_{2,16}$	28858.10	28858.11[b]
$22_{4,18} \rightarrow 21_{5,17}$	24040.08	24039.50[b]
$23_{5,19} \rightarrow 24_{4,20}$	22482.68	22482.51[b]
$24_{5,19} \rightarrow 25_{4,21}$	26776.80	26777.20[b]
$34_{7,27} \rightarrow 35_{6,30}$	25049.31	25049.13[b]

[a] Measured by Crable and Smith

[b] Measured by Sirvetz

TABLE II

SO_2 DISTORTION AND POTENTIAL CONSTANTS

		Iteration Procedure	Least Squares Procedure
τ_{xxxx}	(Mc.)	- 03/617	-0.035615
τ_{zzzz}	"	-10.1548	-10.1557
τ_{zzxx}	"	0 46515	0.46436
τ_{xzxz}	"	-0 061484	-0.048496
f_d	(x 10^{-5} dyne $cm.^{-1}$)	11.3558	13.4146
f_{α/d_o}	" " "	0 7524	0 7614
f_{dd}	" " "	2.7174	2.4628
$f_{d\alpha/d_o}$	" " "	0.2384	0.3288
ν_1 (s)	($cm.^{-1}$)	1361	1445
ν_2 (s)	"	505	506
ν_3 (a)	"	1276	1437

The observed infrared frequencies are 1151, 519, 1361 $cm.^{-1}$ for the ν_1 (s), ν_2 (s) and ν_3 (a) vibration respectively.

Table III

CENTRIFUGAL DISTORTION FREQUENCY SHIFTS (Mc.)

Transition	Calculated on basis of Sets determined by F_{11}: 10.2×10^5 dyne cm.$^{-1}$	10.0×10^5 dyne cm.$^{-1}$	9.8×10^5 dyne cm.$^{-1}$	"Iteration" Procedure (Mc.)	"Least Squares" Procedure (Mc.)	Final Results Combined Infra-red-Microwave Data (Mc.)
$0_{0,0} \rightarrow 1_{1,1}$				-2.45	-2.45	-2.39
$2_{0,2} \rightarrow 2_{1,1}$				-1.77	-1.73	-1.77
$3_{1,3} \rightarrow 4_{0,4}$				-0.31	-0.25	-0.38
$4_{0,4} \rightarrow 4_{1,3}$				+0.15	+0.30	-0.10
$6_{1,5} \rightarrow 5_{2,4}$				-22.84	-23.03	-22.05
$7_{2,6} \rightarrow 8_{1,7}$				+1.85	+2.35	+1.62
$9_{1,9} \rightarrow 8_{2,6}$				-13.43	-12.37	-12.90
$13_{2,19} \rightarrow 12_{3,9}$	-64.67	-52.15	-41.11	-56.15	-54.64	-53.92
$16_{3,13} \rightarrow 17_{2,16}$	+34.16	+21.29	+ 9.96	+27.89	+23.39	+23.11
$22_{4,18} \rightarrow 21_{5,17}$	-225.96	-141.96	-68.21	-155.96	-157.62	-153.84
$23_{5,19} \rightarrow 24_{4,20}$	-24.53	-123.74	-210.39	-117.10	-112.39	-109.75
$24_{5,19} \rightarrow 25_{4,21}$	+59.05	-30.50	-108.88	-16.28	-18.24	-17.86
$34_{7,27} \rightarrow 35_{6,30}$	+160.73	-114.02	-354.40	-79.90	-78.61	-75.25